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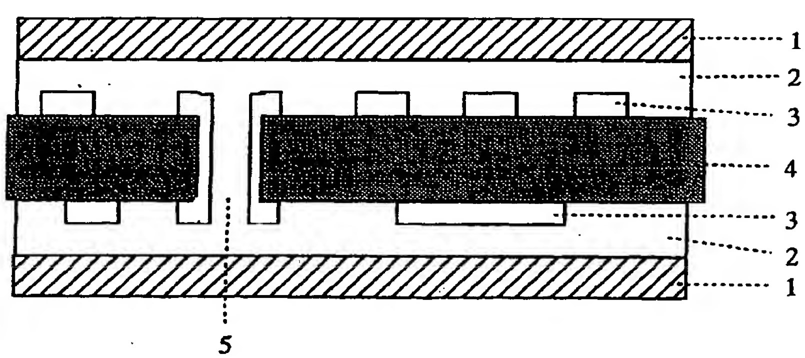
(54) Inter-laminar adhesive film for multi-layer printed wiring board and multi-layer printed wiring board using the same

(57) An inter-laminar adhesive film is provided for multi-layer printed wiring boards, the film being attached to an internal-layer circuit board where the film is embedded in an internal-layer circuit. A process of producing a multi-layer printed wiring board using the film is also provided.

The adhesive film facilitates simultaneous and integral coating of an internal-layer circuit pattern and resin filling into through-holes and/or superficial via holes in a build-up process of producing a multi-layer printed wiring board in which a conductor circuit layer and an insulation layer are alternately laminated together.

The adhesive film for multi-layer printed wiring boards, comprises a support film base and a resin composition which is solid at ambient temperature, both to be laminated on an internal-layer circuit board, wherein the resin composition which is solid at ambient temperature contains at least 10% by weight of a resin with a lower softening point than the lamination thickness of the conductor in the internal-layer circuit and the resin flow of the resin composition at the lamination temperature is at least of the thickness of the conductor of the internal-layer circuit, or is of the depth of a superficial via hole if present in the internal-layer circuit, or is 1/2 fold or more the depth of a through-hole in the internal-layer circuit singly or in combination with a superficial via hole.

Fig. 1



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Description

The present invention relates to an inter-laminar adhesive film for multi-layer printed wiring boards, in particular for carrying out simultaneously the integral coating of an inner-layer circuit pattern and the filling with resin of any superficial via holes and/or through-holes in a multi-layer printed wiring board of the build-up type where a conductive layer and an insulation layer are alternately built up; it also relates to a process of producing a multi-layer printed wiring board using the adhesive film.

As a process of producing a multi-layer printed wiring board, conventionally, a process comprising lamination pressing through several prepreg sheets produced by impregnating an insulation adhesive layer glass cloth impregnated with an epoxy resin to prepare the cloth at B stage and procuring inter-laminar communication through through-holes, has been known. However, the process effects heating and molding under pressure by the use of lamination pressing, so that the process requires large equipment and a long time, and is consequently costly; additionally, the process requires use of glass cloth with a relatively high dielectric constant as the prepreg sheet, which limits the reduction of the inter-laminar thickness, and the process is also problematic because of the insulation concern due to CAF.

As a process for overcoming such problems, recently, attention has been focused on a build-up production technique of multi-layer printed wiring boards, comprising alternately laminating an organic insulation layer on the conductor layer of an internal-layer circuit board. Japanese Patent Laid-open No. 7-202426 and 8-157566 disclose a method for producing a multi-layer printed wiring board, comprising coating and preliminarily drying an underlining adhesive on an internal-layer circuit board with a circuit formed therein and bonding a copper foil or a copper foil with an adhesive on the board. Additionally, in Japanese Patent Laid-open No. 8-64960, it is known a method for producing a multi-layer printed wiring board, comprising coating and preliminary drying of an underlining adhesive and attachment of a film additive adhesive followed by curing under heating, scrubbing with an alkaline oxidant, and plating to form a conductor layer. Because the underlining adhesive layer is formed in an ink form by these methods, however, the possibility of dust contamination into the adhesive layer during the processes is large, which causes circuit failure such as disconnection and short circuit, disadvantageously. As a method with no use of such underlining adhesive, alternatively, Japanese Patent Laid-open No. 7-202418 discloses a method for producing a multi-layer printed wiring board, comprising forming an adhesive layer comprising a high molecular epoxy resin and an epoxy resin in liquids on a copper foil, and attaching the resulting copper foil with the adhesive onto an internal-layer circuit board, but the method is problematic in that the copper foil with the adhesive if used is readily wrinkled or damaged during lamination. Additionally, any of the methods has drawbacks from the respect of workability and characteristic properties in that these methods require a hole filling process by means of a hole filling resin and the like if through-holes are present on an internal-layer circuit board and that voids readily develop in superficial via holes if present any.

The present inventors have made investigations, taking account of the problems described above. The present inven tors have intended to develop an inter-laminar adhesive film for multi-layer printed wiring boards, the adhesive film being capable of integrally carrying out the coating of the internal-layer circuit pattern and the filling of a resin in the superficial via holes and/or through-holes for a build-up process of producing a multi-layer printed wiring board, and a process of producing a multi-layer printed wiring board by using the adhesive film at a high productivity.

In one aspect, the present invention provides an inter-laminar adhesive film for laminating with an internal-layer circuit board of a multi-layer printed wiring board, the film comprising a support film base and a resin composition on said base which is solid at ambient temperature, (eg at 25°C), wherein the resin composition which is solid at ambient temperature contains at least 10% by weight of a resin with a lower softening point than the lamination temperature and is of a thickness larger than the thickness of the electric conductor in the internal-layer circuit and the resin flow of the resin composition at the lamination temperature is at least of the thickness of the electric conductor of the internal-layer circuit, or is of the depth of a superficial via hole if present in the internal-layer circuit, or is 1/2-fold or more the depth of a through-hole if present in the internal-layer circuit singly or in combination with a superficial via hole. In further aspects the invention provides processes of producing a laminate including the adhesive layer and internal-layer circuit board, and for producing a multi-layer printed wiring board including the laminate.

In preferred embodiments of the inter-laminar adhesive film

(1) the resin composition which is solid at ambient temperature comprises the following essential components;

(A) an epoxy resin liquid at ambient temperature;

(B) a polyfunctional epoxy resin with a softening point higher than the lamination temperature and with two or more epoxy groups within the molecule; and

(C) a latent epoxy curing agent initiating a reaction at a temperature higher than the lamination temperature;

and wherein the resin composition may or may not contain a resin which is liquid at ambient temperature other than the component (A) and/or an organic solvent and wherein the resin which is liquid at ambient temperature including the component (A) and /or the organic solvent in total are at 10 to 55 % by weight;

and

(2) the resin composition which is solid at ambient temperature comprises the following essential components;

(A) an epoxy resin which is liquid at ambient temperature;

(B') a polyfunctional epoxy resin with a softening point lower than the lamination temperature and with two or more epoxy groups within the molecule; and

(C) a latent epoxy curing agent initiating a reaction at a temperature higher than the lamination temperature; and

(D) a binder polymer with a weight average molecular weight within a range of 5,000 to 100,000; and

wherein the resin composition may or may not contain a resin liquid at ambient temperature other than the component (A) and/or an organic solvent;

wherein the resin which is liquid at ambient temperature including the component (A) and /or the organic solvent in total are at 10 to 55 % by weight; and

wherein the component (D) is at 5 to 50 % by weight.

Examples of the resin composition which is solid at ambient temperature in accordance with the present invention include a resin composition comprising a thermosetting resin and/or a polymer as the principal component, the resin composition desirably being softened under heating and having a film forming potency and being capable of satisfying the characteristic properties required for inter-laminar insulation materials, such as heat resistance and electric properties, after the composition is thermally set. For example, the composition includes epoxy resins, acrylic resins, polyimide resins, polyamide imide resins, polycyanate resins, polyester resins, and thermosetting polyphenylene ether resins, which may be used as combinations including two or more thereof and may possibly be prepared as an adhesive film layer of a multi-layer structure. Among epoxy resins with a higher reliability and good cost performance as an inter-laminar insulating material, preference is given to the epoxy resin composition of the present invention as described below. Additionally, the thermosetting process can be omitted, if a thermoplastic engineering plastics such as thermoplastic polyimide is used.

The resin composition which is solid at ambient temperature necessarily contains at least 10 % by weight of a resin with a softening point lower than the temperature during lamination. Below 10 % by weight, it is difficult to embed the resin into the through-hole and/or superficial via hole in the internal-layer circuit with no void. Preferably, the resin which is liquid at ambient temperature and/or the resin which is solid at ambient temperature with a softening point lower than the lamination temperature are within a range of 10 to 90% by weight, in total.

The resin composition which is solid at ambient temperature may or may not contain an inorganic component at a preferable content of 30 % by weight or less. Through the addition, an inter-laminar adhesive film for multi-layer printed wiring boards with excellent laser piercing property may be recovered.

In addition to the principal components in the resin composition, use may be made of known and routine additives. For example, use may be made of inorganic fillers such as barium sulfate, calcium carbonate, barium titanate, silicon oxide powder, amorphous silica, talc, clay, and mica powder; flame-retardant agents such as antimony trioxide and antimony pentaoxide; organic fillers such as silicon powder, nylon powder, and fluorine powder; thickening agents such as asbestos, orben, and benton; defoaming agents and/or leveling agents, such as silicon series, fluorine series and polymers and adhesiveness providing agents such as imidazole series, thiazole series, triazole series and silan coupling agents. If necessary, furthermore, use may be made of known and routine coloring agents such as phthalocyanine blue, phthalocyanine green, iodine green, disazo yellow, titanium oxide, and carbon black. In preferred embodiments, the resulting adhesive film may be endowed with excellent laser piercing property, by limiting the inorganic components to 30 % by weight or less in the resin composition. If the inorganic components are above 30 % by weight, vias with small diameters of 100 μm or less have poor shapes after the process of CO_2 laser or UV laser, with the resultant poor plating adhesion, involving a problem of reliability of connection; additionally, the laser processing rate is lowered, disadvantageously, from the respect of productivity.

As to the resin composition which is solid at ambient temperature employed in the inter-laminar adhesive film for multi-layer printed wiring boards of the present invention, a specific embodiment thereof comprising an epoxy resin will now be described below. The "epoxy resin which is liquid at ambient temperature" as a component (A) in accordance with embodiments of the present invention imparts flexibility to the resulting adhesive film and imparts thermal flowability during lamination onto an internal-layer circuit board. More specifically, preference is given to a bisphenol A-type epoxy resin with an epoxy equivalent of about 200, a bisphenol F-type epoxy resin with the same, a phenol novolak-type epoxy resin with the same, or an epoxy-modified fluid rubber or rubber-dispersed fluid epoxy resin. Additionally, those known as reactive diluents such as allylglycidyl ether, glycidyl methacrylate, alkylphenyl glycidyl ether and polyhydric alcohol-type glycidyl ether and those known and for routine use such as alicyclic epoxy resins, may be used singly or in combination with two or more thereof. Together with the

other resin components liquid at ambient temperature described below and the residual organic solvents, these epoxy resins liquid at ambient temperature are preferably within a range of 10 to 55% by weight in the resin composition. Below 10 % by weight, the flexibility and cut processability of the resulting adhesive film are so poor that the film is hardly handled. Above 55 % by weight, alternatively, the fluidity of the adhesive film at ambient temperature is so high that problematic oozing occurs due to edge fusion or a trouble occurs regarding the peelability from the support film and the protective film. A resin component liquid at ambient temperature with a low viscosity should be adjusted less, while such resin component with a high viscosity should be adjusted more. However, the range of adding a scrubbing component corresponding to the component (E) (when present - see claim 5) is limited. Furthermore, the residual organic solvent is within a range of 0.3 to 10% by weight.

The "polyfunctional epoxy resin with two or more epoxy groups within the molecule" as the component (B) or (B') in accordance with the present invention is required to procure various properties such as heat resistance, chemical resistance, and electric properties satisfactory for an inter-laminar insulation material. More specifically, those known and for routine use may be used singly or in combination of two or more, including bisphenol A-type epoxy resin, bisphenol F-type epoxy resin, bisphenol S-type epoxy resin, phenol novolak-type epoxy resin, alkylphenol novolak-type epoxy resin, biphenol-type epoxy resin, naphthalene-type epoxy resin, dicyclopentadiene-type epoxy resin, an epoxylated product of a condensate of phenols with an aromatic aldehyde with phenolic hydroxyl group, triglycidyl isocyanurate, and alicyclic epoxy resin. Furthermore, use is made of the epoxy resins after bromination, so as to impart flame retardancy. These polyfunctional epoxy resins require a component with a softening point higher than the temperature during lamination, whereby the thermal fluidity during attachment can be suppressed and the surface smoothness after heating and curing becomes excellent. Because a polyfunctional epoxy resin liquid at ambient temperature is contained as the component (B'), the range of the addition thereof is limited in the same manner as for the component (A) . The component (B') is a polyfunctional epoxy resin with two or more epoxy groups within the molecule and with a softening point not higher than the lamination temperature, and so, in order to produce an inter-laminar adhesive film for multi-layer printed wiring boards using the component (B'), a binder polymer (D) with an average molecular weight within 5,000 to 100,000 is preferably included in addition to (A) an epoxy resin liquid at ambient temperature and (C) a latent epoxy curing agent initiating a reaction at a temperature higher than the lamination temperature. The resin composition may or may not contain a resin liquid at ambient temperature other than the component (A) and/or an organic solvent, wherein the resin liquid at ambient temperature including the component (A) and/or the organic solvent in total are at 10 to 55 % by weight and the component (D) in the resin composition is at 5 to 50 % by weight.

The component C "latent epoxy curing agent" in accordance with certain embodiments of the present invention includes amine curing agents, guanidine curing agents, imidazole curing agents or epoxy adducts thereof or microcapsulated products thereof, while an epoxy curing agent with a longer pot life below ambient temperature to initiate a reaction at a temperature higher than the temperature during lamination during the elevation of the temperature may preferably be selected, whereby sufficient thermal fluidity during lamination can be maintained to readily determine the conditions for lamination. The reaction initiation temperature is defined as an exothermic peak initiation temperature measured by differential calorimetry (DSC) at a temperature elevation rate of 5 °C/min, provided that 5 parts by weight of a curing agent is added to 100 parts by weight of bisphenol A-type diglycidyl ether (epoxy equivalent: 186 - 192) followed by homogenous dissolution or dispersion. The reaction initiation temperature is for example as follows; dicyandiamide (initiation temperature; 165 - 175 °C), 2-phenyl-4-methyl-5-hydroxymethyl imidazole (initiation temperature; 135 - 145 °C), 2-phenyl-4,5-bis (hydroxymethyl) imidazole (initiation temperature; 145-155 °C), 2,4-diamino-6-(2-methyl-1-imidazoylethyl)-1,3,5-tr iazine (initiation temperature; 110 - 120 °C), 2,4-diamino-6-(2-methyl-1-imidazolylethyl) -1,3,5-triazine• isocyanuric acid adduct (initiation temperature; 125 - 135 °C), and 2,4-diamino-6-(2-undecyl-1-imidazolylethyl)-1,3,5-triazine (initiation temperature; 115 - 125 °C). The amounts of these latent epoxy curing agents to be added are preferably within a range of 2 to 12% by weight of the epoxy resin. Below 2% by weight, curing may be insufficient; above 12% by weight, curing may occur too strongly so that the film gets fragile, unpreferably. If the conditions for the latency and the reaction initiation temperature are met, a phenolic curing agent and a curing promoting agent may also be used, including for example phenol novolak resin, alkylphenol novolak resin and curing promoting agents such as imidazole compounds and organic phosphine compounds, more specifically including tetraphenyl phos-

phonium•tetraphenyl borate and the like. The amount thereof to be added is adjusted as follows; phenolic hydroxyl group should be within 0.6 to 1.0 equivalent to the epoxy group in the epoxy resin; the curing promoting agent should be at 0.5 to 2 % by weight to the total of the two resins. Furthermore, the individual latent epoxy curing agents described above may be used singly or in combination of two or more thereof or in combination with known curing promoting agents for routine use.

So as to improve the mechanical strength and flexibility of preferred embodiments of the adhesive film for better handling, the component (D), namely "binder polymer with a weight average molecular weight within a range of 5,000 to 100,000" is desirable. If the weight average molecule weight is below 5,000, the effect thereof on improving the mechanical strength and flexibility cannot be exerted; above 100,000, the solubility thereof in an organic solvent and the miscibility thereof with an epoxy resin are deteriorated, so that the resulting film cannot be used. Preferably, the amount thereof to be added is within a range of 5 to 50 % by weight. Below 5 % by weight, the effect thereof on improving the mechanical strength and flexibility cannot be exerted; above 50 % by weight, alternatively, the thermal fluidity of the resulting film is deteriorated, unpreferably. Because the thermal fluidity of the resulting film can be suppressed when the film contains the component, the polyfunctional epoxy resin with a softening point higher than the laminate temperature is not essential. Additionally, the binder polymer has an effect of preventing cissing over the support film. More specifically, the binder polymer includes (brominated) phenoxy resin, polyacrylic resin, polyimide resin, polyamide imide resin, polycyanate resin, polyester resin, and thermosetting polyphenylene ether resin. These may possibly be used in combination of two or more thereof.

If it is desired to efficiently effect a chemical process with an oxidant, as a type of wet scrubbing, on the film surface after the adhesive film is cured under heating, at least one scrubbing component selected from oxidant-soluble rubber components, amino resin, inorganic filler and organic filler is necessary. Examples of the rubber components include polybutadiene rubber, polybutadiene rubber after various modification such as epoxy modification, urethane modification, and (metha)acrylonitrile modification and further includes (metha)acrylonitrile•butadiene rubber containing carboxyl groups and epoxy resins of acrylic rubber-dispersed type. The amino resin includes melamine resin, guanamine resin, urea resin and alkyl etherified resins thereof. The inorganic filler includes calcium carbonate, magnesium carbonate and magnesium oxide; the organic filler includes powdery epoxy resin and crosslinked acrylic polymer, and additionally includes the aforementioned amino resins after thermal curing and fine grinding. These scrubbing components are importantly within a range of 5 to 40 % by weight in the resin composition. Below 5 % by weight, the scrubbing potency is not sufficient; above 40 % by weight, the electric properties, chemical resistance and thermal resistance of the resulting film are so poor that the film cannot be used practically as an inter-laminar insulation material.

Also the additives to the resin composition may include a component (F) which is a catalyst for non-electro-plating with metal, to provide an inter-laminar adhesive film having good properties for wet plating. The examples of the catalyst include a metal powder such as palladium, gold, platinum, silver, copper, cobalt, tir and/or its halide, oxide, hydroxide, sulfide, peroxide, amine salt, sulfate, nitrate, salt of organic acid, chelate thereof. An inorganic material coated with such metal(s) and/or its compound are preferably used as catalyst. The examples of the inorganic materials include powder of alumina or carbon and so on. The diameter of the powder may be within a range of from 0.1 to 50μm. The catalyst is preferably within a range of 0.05 to 3% by weight in the resin composition.

An inter-laminar adhesive film of a two-layer structure for multi-layer printed wiring boards, with no such upper limit of the scrubbing component, may be produced by laminating together a scrubbable resin composition which is solid at ambient temperature, essentially comprising the following components;

(a) a polyfunctional epoxy resin with two or more epoxy groups within the molecule;
(b) an epoxy curing agent; and
(C) at least one scrubbing component selected from the group consisting of a rubber component, an amino resin, an inorganic filler and an organic filler,

and the resin composition described above in accordance with the present invention, whereby the surface scrubbing potency with an oxidant and the reliability as an inter-laminar insulation material can be imparted in a simple fashion to resulting adhesive film. The thickness of the scrubbable resin composition is preferably less than the half of the total film thickness within a range of 1 to 15 μm, from the respect of the flexibility and fine patterning of the resulting film and the reliability of the inter-laminar insulation. As the polyfunctional epoxy resin to be used as the component (a), use is made of those described above, with no mention that they are in liquids or in solids; as the epoxy curing agent, use is made of known curing agents for routine use, such as curing agents of amines, guanidines, imidazoles and acid anhydrides or epoxy adducts thereof. As the scrubbing agent, use is made of the same one as the component (E) at 5% by weight or more.

And the catalyzer for non-electro-plating with metal (F) is added to the resin composition at 0.05% by weight or more.

The inter-laminar adhesive film for multi-layer printed wiring boards in accordance with the present invention can

be prepared by coating a resin varnish dissolved in a given organic solvent using a base film as a support, drying the solvent by heating and/or hot air spraying to prepare a resin composition in solids at ambient temperature. The support base film includes polyolefins such as polyethylene and polyvinyl chloride; polyesters such as polyethylene terephthalate; polycarbonate; furthermore, release paper and metal foils such as copper foil and aluminium foil. The thickness of the support base film is generally 10 to 150 μm. The support base film is further processed with release process other than mud process and corona process. As the organic solvent, use may be made of ketones such as acetone, methyl ethyl ketone, and cyclohexane; acetate esters such as ethyl acetate, butyl acetate, Cellosolve acetate, propylene glycol monomethyl ether acetate, and Carbitol acetate; Cellosolves such as Cellosolve and butyl Cellosolve; Carbitols such as Carbitol and butyl Carbitol; aromatic hydrocarbons such as toluene and xylene; and additionally, dimethylformamide, dimethylacetoamide, and N-methyl pyrrolidone, singly or in combination with two or more thereof. The amount of the residual organic solvent is defined as weight decrement ratio, prior to and after drying in a dryer kept at 200 °C for 30 minutes.

The thickness of the resin composition which is solid at ambient temperature is above the thickness of the conductor on the internal-layer circuit board to be laminated, and varies depending on factors such as the residual copper ratio in the internal-layer circuit pattern, the board thickness, the through-hole diameter, the superficial via hole diameter, the number of holes and the preset value of the thickness of the insulation layer. Generally, the thickness is within a range of the conductor thickness plus (10 to 120 μm). If the board thickness is large and the resin filled volume of the through-hole is large, a thicker resin composition is necessary. The thus recovered adhesive film of the present invention, comprising the resin composition solid at ambient temperature and the support base film, is stored as it is or is stored after a protective film is further laminated on the other face of the resin composition and is then rolled in. Such protective film includes the same as for the support base film, for example, polyolefin such as polyethylene, polyvinyl chloride, and polypropylene; polyester such as polyethylene terephthalate; and release paper. The thickness of the protective film is generally 10 to 100 μm. Furthermore, the protective film may satisfactorily be processed at a release process in addition to mud process and emboss process. As described below, the resin in the resin composition oozes during lamination, so that a part by weight the support base film should be arranged at a width of about 5 mm or more on both ends or single end of the roll, whereby the prevention of resin adhesion onto the laminate part and the peeling of the support base film can readily be done, advantageously.

With reference to the accompanying drawings, embodiments of the multi-layer printed wiring board using the inter-laminar adhesive film for multi-layer printed wiring boards and a process of fabricating the board will now be described by way of example only. For attaching the adhesive film of the present invention onto a pattern processed internal-layer circuit board, the protective film if present is removed, and then, the resin composition which is solid at ambient temperature is laminated under pressure and heating (Fig. 1). By carrying out the lamination under conditions such that the extent of resin flow during lamination is above the thickness of the conductor of the internal-layer circuit and above the half of the through-hole depth and/or the superficial via hole depth of the internal-layer circuit, the coating of the internal-layer circuit pattern and the resin filling in the superficial via hole can be done simultaneously and integrally. As the internal-layer circuit board, use is made of glass epoxy- and metal boards, polyester boards, polyimide boards, thermosetting polyphenylene ether boards and the like. The circuit surface may preliminarily be subjected to a scrubbing process, satisfactorily. Under reduced pressure, the lamination is effected by batch-wise process or continuously by means of roll. And preferably, both the surfaces are laminated. As described above, the lamination conditions vary, depending on the thermal melt viscosity and thickness of the resin composition in solids at ambient temperature of the present invention, the through-hole diameter and depth of the internal-layer circuit board, and/or the superficial via hole diameter and depth. Generally, the temperature for contact bonding is 70 to 200 °C; and the pressure therefor is 1 to 10 kgf/cm^2. Lamination is done under reduced pressure of 20 mmHg or less. If the through-hole diameter is large and deep or if the board is of a larger thickness, the resulting resin composition is so thick to require lamination conditions at a high temperature and/or a high pressure. Generally, a board thickness up to about 1.4 mm and a through-hole diameter up to about 1 mm are appropriate for good resin filling. The surface smoothness of the resin composition after lamination is better as the support base film is thicker, which is nevertheless disadvantageous for embedding the resin in between the circuit pattern with no void. Preferably, therefore, the support base film is of a thickness of the conductor thickness plus or minus 20 μm. When the surface smoothness and thickness of the resin on the pattern are not sufficient because the conductor thickness on the internal-layer circuit is thick or when recess develops in the hole because the diameters of the through-hole and the superficial via hole are large, the inter-laminar adhesive film for multi-layer printed wiring boards should be further laminated thereon, to possibly cope with various conductor thickness and board thickness. After lamination, the film is cooled around ambient temperature, to peel off the support base film.

After laminating the inter-laminar adhesive film for multi-layer printed wiring boards (Fig.2), the resin composition is thermally cured if necessary, and then, a copper foil with an adhesive or a copper foil is further laminated as an upper layer thereof under heating, thereafter integrating them all, to prepare a multi-layer printed wiring board. The curing conditions under heating vary, depending on the types of materials of the internal-layer circuit board and the curing

temperature of the copper foil with an adhesive if used, and the conditions are selected within ranges of 120 to 200 °C and 20 to 90 minutes.

For an adhesive film for multi-layer printed wiring boards according to claim 6 or 8, the adhesive film of the present invention is laminated on an internal-layer circuit board with a pattern processed, in the same manner as described above, so that the resin composition containing the scrubbing component or catalyzer might be on the outer side (Figs. 3 and 4). Thereafter, if necessary, the film is cured under heating, and a given through-hole and/or via hole part is pierced by laser or drilling, and the surface of the resin composition is scrubbed at wet and/or dry process, if necessary. Then, the conductor layer is formed by dry plating and/or wet plating, to prepare a multi-layer printed wiring board. The thermally curing conditions are selected within ranges of 120 to 200 °C and 10 to 90 minutes. The dry scrubbing process of the surface of the resin composition includes mechanical polishing with puff, sandblast, etc. and plasma etching and the like. Alternatively, the wet scrubbing process includes chemical processes with oxidants such as permanganese salts, dichromate salts, ozone, perhydrogen oxide/sulfuric acid, nitric acid and the like. When an adhesive film containing scrubbing component soluble in an oxidant or an adhesive film of a two-layer structure with a scrubbable resin composition formed on the surface is attached, the scrubbing process with oxidants can be efficiently carried out. After preparing an anchor with protrusions and recesses on the surface of the resin composition, if necessary, a conductor layer is formed through dry plating such as vapor deposition, sputtering and ion plating and/or wet plating such as non-electrolytic or electrolytic plating. For an adhesive film for multi-layer printed wiring boards according to claim 6 or 8, the adhesive film of the present invention is laminated on an internal-layer circuit board with a pattern processed, in the same manner as described above, so that the resin composition containing the scrubbing component or the catalyzer for non-electro-plating with metal might be on the outer side (Figs 3 and 4).

The resin composition including the catalyst for non-electro-plating with metal is preferably one for additive method which produces an inter-laminar adhesive film for multi-layer printed wiring boards because of using for non-electro-plating.

Then, a plated resist with a pattern reverse to that of a conductor layer may be formed, to form the conductor layer only through non-electrolytic plating. After the conductor layer is thus formed, followed by annealing process at 130 to 200 °C for 10 to 60 minutes, the curing of the thermosetting resin progresses so that the via strength of the conductor layer can be further improved.

A multi-layer printed wiring board produced by using the inter-laminar adhesive film for multi-layer printed wiring boards of the present invention has so excellent surface smoothness, that the process as described above can be repeated plural times to laminate a build-up layer at multiple steps, to prepare a multi-layer printed wiring board.

[Examples]

The present invention will be described specifically in the following production examples, examples and comparative examples, but the invention is not limited to these examples. The assessment method is as follows.

<Flowability at 1/2 depth of through-hole, through-hole embedding, via hole embedding, and embedding of conductor thickness in between circuit>

Under observation of resin shape on cross section. The term "good" means the state where resin is filled in the hole or in between the circuit.

<Plane smoothness on circuit>

The surface roughness on the circuit of A and B coupons defined according to the IPC standard was measured according to JISB 0601.

<Heat resistance of solder>

After immersion in a solder bath at 260 °C for 60 seconds, the immersed matter was drawn up to observe visually the solder status. The term "good" means no abnormality in the solder status.

[Example 1]

Thirty parts by weight of a fluid bisphenol A-type epoxy resin (with an epoxy equivalent of 185, Epicoat 828 EL manufactured by Oil Shell Epoxy, Co., Ltd.) as the component A (the amount to be blended is hereinafter represented in part by weight), 20 parts by weight of a bisphenol A-type epoxy resin (with an epoxy equivalent of 2000 and a softening point of 124 °C, Epiclon 7051 manufactured by Dai-Nippon Ink Chemistry, Co., Ltd.) as the component B,

and 40 parts by weight of a brominated bisphenol A-type epoxy resin (with an epoxy equivalent of 499 and a softening point of 75 °C and a bromide content of 21 % by weight, YDB-500 manufactured by Toto Chemical Industry, Co., Ltd.) were dissolved in methyl ethyl ketone (abbreviated as MEK hereinafter) under heating and agitation, to which were added epoxy curing agents as the component (C), namely 4 parts by weight of 2,4-diamino-6-(2-methyl-1-imidazolylethyl)-1,3,5-triazine•isocyanuric acid adduct, 2 parts by weight of finely ground silica and 4 parts by weight of antimony trioxide, to prepare a resin composition varnish. The varnish was coated on a polyethylene terephthalate (abbreviated as PET hereinafter) film of a thickness of 30 μm to a final dried thickness of 50 μm by means of a roller coater, followed by drying at 80 to 100 °C for 10 minutes, to prepare an adhesive film (at a content of the residual solvents at 0.5 % by weight). The film was folded at an angle of 180 degrees so as to assess the flexibility, and no abnormality such as crack was found in the resin part.

[Example 2]

Twenty parts by weight of a fluid bisphenol A-type epoxy resin (Epicoat 828 EL manufactured by Oil Shell Epoxy, Co., Ltd.) as the component A, 20 parts by weight of a brominated bisphenol A-type epoxy resin (YDB-500, manufactured by Toto Chemical Industry, Co., Ltd.) and 20 parts by weight of cresol novolak-type epoxy resin (with an epoxy equivalent of 215 and a softening point of 78 °C; Epiclon N-673, manufactured by Dai-Nippon Ink Chemistry, Co., Ltd.) as the component B', and 15 parts by weight of a polybutadiene rubber with its terminus epoxylated (Denalex R-45EPT, manufactured by Nagase Chemical Industry, Co., Ltd.) were dissolved in MEK under heating and agitation, to which were added 50 parts by weight of a brominated phenoxy resin varnish (at a non-volatile content of 40 % by weight and a bromide content of 25 % by weight and the solvent composition of xylene : methoxypropanol : methyl ethyl ketone = 5 : 2 : 8, YPB-40-PXM40 manufactured by Toto Chemical Industry, Co., Ltd.) as the component (D), epoxy curing agents as the component (C), namely 4 parts by weight of 2,4-diamino-6-(2-methyl-1-imidazolylethyl)-1,3,5-triazine•isocyanuric acid adduct, and 2 parts by weight of finely ground silica and 4 parts by weight of antimony trioxide, and 5 parts by weight of calcium carbonate as the component (E), to prepare a resin composition varnish. The varnish was coated on a PET film of a thickness of 38 μm to a final dried thickness of 70 μm by means of a roller coater, followed by drying at 80 to 100 °C for 12 minutes, to prepare an adhesive film (at a content of the residual solvents at 2 % by weight). The film was folded at an angle of 180 degrees so as to assess the flexibility, and no abnormality such as crack was found in the resin part.

[Example 3]

The resin composition varnish as described in Example 2 was coated on a PET film of a thickness of 50 μm to a final dried thickness of 100 μm by means of a roller coater, followed by drying at 80 to 120 °C for 15 minutes, to prepare an adhesive film (at a content of the residual solvents at 4 % by weight). The film was folded at an angle of 180 degrees so as to assess the flexibility, and no abnormality such as crack was found in the resin part.

[Example 4]

Fifty parts by weight of a brominated bisphenol A-type epoxy resin (YDB-500 manufactured by Toto Chemical Industry, Co., Ltd.) as the component (a) and 25 parts by weight of a polybutadiene rubber with its terminus epoxylated (Denalex R-45EPT manufactured by Nagase Chemical Industry, Co., Ltd.) as the component (c) were dissolved in MEK under heating and agitation, to which were added epoxy curing agents as the component (b), namely 3 parts by weight of 2-ethyl-4-methyl imidazole, 2 parts by weight of finely ground silica and 20 parts by weight of calcium carbonate as the component (c), to prepare a resin composition varnish. The varnish was coated on a PET film of a thickness of 38 μm to a final dried thickness of 5μm by means of a roller coater, followed by drying at 80 to 100 °C for 5 minutes for semi-curing, to prepare a scrubbable resin composition (at a content of the residual solvents at less than 0.1 % by weight). Furthermore, the resin composition varnish from Example 1 was coated thereon to a final dried thickness of 60 μm by means of a roller coater, followed by drying at 80 to 100 °C for 12 minutes, to prepare an adhesive film of a two-layer structure comprising resin compositions (at a content of the residual solvents of 1.5 % by weight). The film was folded at an angle of 180 degrees so as to assess the flexibility, and no abnormality such as crack was found in the resin part.

[Example 5]

Forty-five parts by weight of a thermosetting allylated polyphenylene ether resin and 15 parts by weight of diallyl phthalate monomer as the component (D), 10 parts by weight of a fluid bisphenol A-type epoxy resin (Epicoat 828 EL manufactured by Oil Shell Epoxy, Co., Ltd.) as the component (A), and 20 parts by weight of a cresol novolak type

epoxy resin (Epiclon N-673, manufactured by Dai-Nippon Ink Chemistry, Co., Ltd.) as the component B' were dissolved in MEK under heating and agitation, to which were added 2 parts by weight of dicyandiamide, 0.5 part by weight an organic peroxide (Perbutyl P, manufactured by Nippon Yushi, Co., Ltd.), 2 parts by weight of finely ground silica and 0.5 part by weight a silicon leveling agent as the epoxy curing agents as the component C, to prepare a resin composition varnish. In the same manner as in Example 4, a scrubbable resin composition of a thickness of 5 μm was formed on a PET film. Still further, the resin composition varnish was coated thereon to a final dried thickness of 70 μm by means of a roller coater, followed by drying at 80 to 100 °C for 12 minutes, to prepare an adhesive film of a two-layer structure comprising the resin compositions (at a content of the residual solvents at 2.5 % by weight). The film was folded at an angle of 180 degrees so as to assess the flexibility, and no abnormality such as crack was found in the resin part.

[Example 6]

Ten parts by weight of a fluid bisphenol A-type epoxy resin (Epicoat 828 EL manufactured by Oil Shell Epoxy, Co., Ltd.) and 60 parts by weight of a brominated bisphenol A-type epoxy resin (YDB-500, manufactured by Toto Chemical Industry, Co., Ltd.) as the component (a) were dissolved in MEK under heating and agitation, to which were added 2 parts by weight of 2-ethyl-4-methyl imidazole as the epoxy curing agents as the component (b), 2 parts by weight of a finely ground silica and as the component (c), 2 parts by weight of Pd and PdC12 mixed powder (Pd:PdCl2=1:1 by weight), to prepare a resin composition varnish. The resin composition varnish was coated on a PET film to a final dried thickness of 5 μm by means of roller coater, followed by drying at 80 to 100°C, for 5 minutes, to prepare an additive resin composition film (the amount of residual solvents was below 0.1% by weight). Furthermore, the resin composition varnish from Example 1 was coated final dried thickness of 60 μm by means of a roller coater, followed by drying at 80 to 100°C, for 12 minutes, to prepare an adhesive film of a two-layer structure comprising resin composition. (The amount of the residual solvents was 1.5% by weight) .

The film was folded at an angle of 180 degrees so as to assess the flexibility, and no abnormality such as crack was found in the resin parts.

[Production Example 1]

The adhesive film recovered in Example 1 was laminated simultaneously on both the surfaces of each of the glass epoxy internal-layer circuit boards shown in Table 1. Preferable conditions for filling resins in through-holes with no void were as follows; for continuous process, the roll temperature was 100 °C; the pressure, 3 kgf/cm^2; the rate, 30 cm/minute and the vapor pressure, 2 mmHg or less; for batch process, the roll temperature was 80 °C; the pressure, 1 kgf/cm^2; the vapor pressure was 2 mmHg or less after 5-sec pressing. After left to stand around ambient temperature, the PET film was peeled off, and then, a commercially available copper foil with an adhesive was attached thereon for integral curing at 170 °C for 60 minutes, to prepare a four-layer printed wiring board. Thereafter, a given through-hole part and a given via hole part were pierced with a drill and/or laser, followed by non-electrolytic and/or electrolytic plating, to prepare a four-layer printed wiring board according to subtractive process. The resulting printed wiring board was soldered at 260 °C for 60 seconds, and the heat resistance against soldering was observed, with no abnormality.

[Production Example 2]

The adhesive film recovered in Example 2 was laminated simultaneously on both the surfaces of each of the glass epoxy internal-layer circuit boards shown in Table 1, by means of a vacuum laminator. Preferable conditions for filling resins in through-holes with no void were as follows; for continuous process, the roll temperature was 110 °C; the pressure, 3 kgf/cm^2; the rate, 30 cm/minute and the vapor pressure, 30 mmHg or less; for batch process, the roll temperature was 85 °C; the pressure, 1 kgf/cm^2; the vapor pressure was 2 mmHg or less after 5-sec pressing. After left to stand around ambient temperature, the PET film was peeled off followed by thermal curing at 150 °C for 30 minutes, and thereafter, a given via hole part by weight ϕ0.10 was pierced with CO_2 laser. Then, the surface of the resin composition was subjected to a scrubbing process with an alkaline oxidant of permanganese salt, and on the whole surface was formed a conductor layer through non-electrolytic and/or electrolytic plating, to prepare a four-layer printed wiring board according to subtractive process. Subsequently, the board was subjected to annealing process at 150 °C for 30 minutes, so as to stabilize the adhesion strength of the conductor. The via strength of the conductor was 1.0 kg/cm or more. The resulting printed wiring board was soldered at 260 °C for 60 seconds, and the heat resistance against soldering was observed, with no abnormality.

[Production Example 3]

The adhesive film recovered in Example 3 was laminated simultaneously on both the surfaces of each of the glass

epoxy internal-layer circuit boards shown in Table 1, by means of a vacuum laminator. Preferable conditions for filling resins in through-holes with no void were as follows; for continuous process, the roll temperature was 110 °C; the pressure, 3 kgf/cm^2; the rate, 25 cm/minute and the vapor pressure, 30 mmHg or less; for batch process, the roll temperature was 90 °C; the pressure, 1 kgf/cm; the vapor pressure was 2 mmHg or less after 6-sec pressing. After left to stand around ambient temperature, the PET film was peeled off followed by thermal curing at 150 °C for 30 minutes, and thereafter, a given via hole part by weight ϕ0.10 was pierced with CO_2 laser. Then, the surface of the resin composition was subjected to a scrubbing process with an alkaline oxidant of permanganese salt, to form a plated resist of a reverse pattern to that of the conductor layer, to prepare a four-layer printed wiring board according to additive process. Subsequently, the board was subjected to annealing process at 150 °C for 60 minutes, so as to stabilize the adhesion strength of the conductor. The via strength of the conductor was 1.0 kg/cm or more. The resulting printed wiring board was soldered at 260 °C for 60 seconds, and the heat resistance against soldering was observed, with no abnormality.

[Production Example 4]

The adhesive film recovered in Example 4 was laminated simultaneously on both the surfaces of each of the glass epoxy internal-layer circuit boards shown in Table 1, by means of a vacuum laminator. Preferable conditions for filling resins in through-holes with no void were as follows; for continuous process, the roll temperature was 100 °C; the pressure, 3 kgf/cm^2; the rate, 30 cm/minute and the vapor pressure, 30 mmHg or less; for batch process, the roll temperature was 80 °C; the pressure, 1 kgf/cm^2; the vapor pressure was 2 mmHg or less after 5-sec pressing. After left to stand around ambient temperature, the PET film was peeled off followed by thermal curing at 170 °C for 30 minutes, and thereafter, a given via hole part and a given through-hole part were pierced with a drill and/or laser. Then, the surface of the resin composition was subjected to a scrubbing process with an alkaline oxidant of permanganese salt, and on the whole surface was formed a conductor layer through non-electrolytic and/or electrolytic plating, to prepare a four-layer printed wiring board according to subtractive process. The via strength of the conductor was 1.0 kg/cm or more. The resulting printed wiring board was soldered at 260°C for 60 seconds, and the heat resistance against soldering was observed, with no abnormality.

[Production Example 5]

The adhesive film recovered in Example 5 was laminated simultaneously on both the surfaces of each of the glass epoxy internal-layer circuit boards shown in Table 1, by means of a vacuum laminator. Preferable conditions for filling resins in through-holes with no void were as follows; for continuous process, the roll temperature was 120 °C; the pressure, 3 kgf/cm^2; the rate, 35 cm/minute and the vapor pressure, 30 mmHg or less; for batch process, the roll temperature was 95 °C; the pressure, 1 kgf/cm^2; the vapor pressure was 2 mmHg or less after 6-sec pressing. After left to stand around ambient temperature, the PET film was peeled off, followed by thermal curing at 180 °C for 60 minutes, and thereafter, a given via hole part and a given through-hole part were pierced with a drill and/or laser. Then, the surface of the resin composition was subjected to a scrubbing process with an alkaline oxidant of permanganese salt, to form a plated resist of a reverse pattern to that of the conductor layer, to prepare a four-layer printed wiring board according to additive process. The via strength of the conductor was 1.0 kg/cm or more. The resulting printed wiring board was soldered at 260 °C for 60 seconds, and the heat resistance against soldering was observed, with no abnormality.

[Production Example 6]

By means of a vacuum laminator, the adhesive film recovered in Example 2 was laminated simultaneously on both the faces of an internal-layer circuit board comprising the four-layer printed wiring board recovered in the Production Example 2, being of a board thickness of 0.9 mm and a conductor thickness of 25 μm and with a superficial via hole of ϕ0.10. Preferable conditions for filling resins in the superficial via hole with no void were as follows; for continuous process, the roll temperature was 110 °C; the pressure, 1.5 kgf/cm^2; the rate, 25 cm/minute and the vapor pressure, 30 mmHg or less; for batch process, the temperature was 85 °C; the pressure, 1 kgf/cm^2; the vapor pressure was 2 mmHg or less after 5-sec pressing. After left to stand around ambient temperature, the PET film was peeled off followed by thermal curing at 150 °C for 30 minutes. Thereafter, a given via hole part of ϕ0.10 and the like were pierced with CO_2 laser. Then, the surface of the resin composition was subjected to a scrubbing process with an alkaline oxidant of permanganese salt, and then, non-electrolytic and/or electrolytic copper plating was done on the whole surface thereof, to prepare a conductor layer. Subsequently, a pattern was formed according to subtractive process, followed by annealing process at 150 °C for 30 minutes, to prepare a six-layer printed wiring board. The via strength of the conductor was 1.0 kg/cm or more. The resulting printed wiring board was soldered at 260 °C for 60 seconds, and the

heat resistance against soldering was observed, with no abnormality.

[Production Example 7]

The adhesive film recovered in Example 2 was laminated simultaneously on both the faces of each of the internal-layer circuit boards shown in Table 1 by means of a vacuum laminator, in the same manner as in the Production Example 2. The PET film was peeled off followed by thermal curing at 150 °C for 30 minutes. Thereafter, a given via hole part by weight ϕ0.10 was pierced with CO_2 laser. Then, a copper foil of a thickness of 0.2 μm was formed on the resin composition by sputtering process, followed by formation of a conductor layer on the whole surface by electrolytic copper plating, to prepare a four-layer printed wiring board by subtractive process, followed by annealing process at 150 °C for 30 minutes, so as to stabilize the adhesion strength of the conductor. The via strength of the conductor was 1.0 kg/cm or more. The resulting printed wiring board was soldered at 260°C for 60 seconds, and the heat resistance against soldering was observed, with no abnormality.

[Production Example 8]

The adhesive film recovered in Example 6 was laminated simultaneously on both the surfaces of each of the glass epoxy internal-layer circuit boards shown in Table 1, by means of a vacuum laminator. Preferable conditions for filling resins in through-holes with no void were as follows; for continuous process, the roll temperature was 100°C; the pressure, 3 kgf/cm^2; the rate, 30 cm/minute and the vapour pressure, 30 mmHg or less; for batch process, the roll temperature was 80°C; the pressure, 1 kgf/cm^2; the vapour pressure was 2 mmHg or less after 5-sec pressing. After left to stand around ambient temperature, the PET film was peeled off followed by thermal curing at 170°C for 30 minutes, and thereafter, a given via hole part and a given through-hole part were pierced with a drill and/or laser. Then, the surface of the resin composition was subjected to desmear process with an alkaline oxidant of permanganese salt, and on the whole surface was formed a conductor layer through non-electrolytic and/or electrolytic plating, to prepare a four-layer printed wiring board according to additive process. The via strength of the conductor was 1.0 kg/cm or more. The resulting printed wiring board was soldered at 260°C for 60 seconds, and the heat resistance against soldering was observed, with no abnormality.

[Comparative Examples 1 and 2]

In the same manner as in Example 1, an adhesive film was recovered (at a residual solvent content of 0.5 % by weight), except that the amount of the fluid bisphenol A-type epoxy resin as the component (A) to be added was reduced to 5 parts (Comparative Example 1) or was elevated to 120 parts (Comparative Example 2). For assessing the flexibility, the resulting film of Comparative Example 1 (at a fluid content of 7 % by weight) was folded at an angle of 180 degrees. Cracking occurred in the adhesive layer, and due to such insufficient flexibility, the film was handled with much difficulty. The film of Comparative Example 2 (at a content of the fluid component being 63 % by weight) was highly fluid at ambient temperature, involving oozing because of edge fusion, so that the film could not be handled as film.

[Comparative Example 3]

In the same manner as in Example 1, an adhesive film was recovered (at a residual solvent content of 0.5 % by weight), except that the whole amount of the bisphenol A-type epoxy resin (Epiclon 7051 manufactured by Dai-Nippon Ink Chemistry, Co., Ltd.) as the component (B) was replaced with 60 parts by weight of a brominated bisphenol A-type epoxy resin (YDB-500 manufactured by Toto Chemical Industry, Co., Ltd.) . For assessing the flexibility, the resulting film was folded at an angle of 180 degrees. No abnormality including cracking occurred in the resin part.

[Comparative Example 4]

In the same manner as in Example 2, an adhesive film was recovered (at a residual solvent content of 2 % by weight; 42 % by weight of the scrubbing component and 36 % by weight of the inorganic component as the (E)), except that the amount of calcium carbonate as the component (E) was elevated to 50 parts by weight. For assessing the flexibility, the resulting film was folded at an angle of 180 degrees. No abnormality including cracking occurred in the resin part.

[Comparative Production Example 1]

The adhesive film recovered in the Comparative Example 1 was laminated simultaneously on both the faces of

the same glass epoxy internal-layer circuit board as in the Production Example 1, by means of a vacuum laminator. Under the same lamination conditions as in the Production Example 1, namely at a roll temperature of 100 °C and a rate of 30 cm/minute for continuous process and at a temperature of 80 °C for batch process, the laminate temperature of the resin composition of the adhesive film was less than 75 °C. At the Maximum roll pressure of 8 kgf/cm^2 for continuous process and at the maximum roll pressure of 6 kgf/cm^2 for batch process, voids remained in the throught-hole, which could not be filled with the resin.

[Comparative Production Example 2]

The adhesive film recovered in the Comparative Example 3 was laminated simultaneously on both the faces of the same glass epoxy internal-layer circuit board as in the Production Example 1, by means of a vacuum laminator. Under the same lamination conditions as in the Production Example 1, resin oozing occurred strongly, so that the film could not be laminated at a uniform resin thickness on the internal-layer circuit. Additionally, resin cissing occurred on the conductor during curing under heating, so that a more non-uniform thickness is caused.

[Comparative Production Example 3]

The adhesive film recovered in the Comparative Example 4 was laminated simultaneously on both the faces of the same glass epoxy internal-layer circuit board as in the Production Example 2, by means of a vacuum laminator. Preferable conditions for filling resins in through-holes with no void were as follows; for continuous process, the roll temperature was 115 °C; the pressure, 3 kgf/cm^2; the rate, 25 cm/minute and the vapor pressure, 30 mmHg or less; for batch process, the roll temperature was 90 °C; the pressure, 1 kgf/cm^2; the vapor pressure was 2 mmHg or less after 5-sec pressing. After left to stand around ambient temperature, the PET film was peeled off, for subsequent curing at 150 °C for 30 minutes. Thereafter, a given through-hole part of ϕ0.10 was pierced with CO2 laser. The opening of the via was at about 0.10 mm, but the bottom was less than the half, and the via side wall was fragile, which means no reliability in the plating process. Additionally, piercing of a via hole of ϕ0.10 was attempted by means of UV laser, but compared with the film of Example 2, the resulting via side wall was dirty and the processing time was long. Then, the surface of the adhesive was subjected to scrubbing process with an alkaline oxidant of permanganese salt, to form a conductor layer on the whole surface by non-electrolytic and/or electrolytic plating and prepare then a four-layer printed wiring board according to subtractive process. The resulting via strength of the conductor was 1.0 kg/cm or more. The printed wiring board was soldered at 260 °C for 60 seconds, and the heat resistance against soldering was observed. Abnormality including expansion and conductor peeling was observed.

[0042]

[Table 1]

Production Examples	1	1	3	4	5	6	7	Comparative Example 1	Comparative Example 2	Comparative Example 3	8
Internal-layer circuit board used											
circuit board thickness (mm)	0.6	0.8	1	0.8	0.8	0.9	0.8	0.6	0.6	0.8	0.8

circuit conductor thickness (μm)	30	30	45	35	45	25	30	30	30	30	30
through-hole (pore diameter in mm)	0.3	0.3 & 0.6	0.3 & 0.6	0.3 & 0.6	0.3 & 0.6	none	0.3 & 0.6	0.3	0.3	0.3 & 0.6	0.3& 0.6
via hole	none	none	none	none	noe	present	none	none	none	none	none
Resin composition in solids at ambient temperature used											
film production (Example No.)	1	2	3	4+1	5+1	2	2	Comparative Example 1	Comparative Example 3	Comparative Example 4	8
film thickness (μm)	50	70	100	5+60	5+70	70	70	50	50	70	5+60

Support base film material (μm)	PET(30)	PET(38)	PET(50)	PET(38)	PET(38)	PET(38)	PET(38)	PET(30)	PET(30)	PEC(38)	PET(38)
Printed wiring board											
layer structure	4 layer	4 laye	4 layer	4 layer	4 layer	6 layer	4 layer	not practiced	not practiced	4 layer	4 layer
Through-hole 1/2 depth fluidity	good	good	good	good	good	good	good	poor	good	good	good
Through-hole embedding (0.3 mm)	good	good	good	good	good	not practiced	good	poor	good	good	good
(0.6 mm)	not practiced	good	good	good	good	not practiced	good	not practiced	not practied	good	good

Via hole embedding	not practiced	not practiced	not practiced	not practiced	not practiced	good	not practiced	not practiced	not practiced	not practiced	not practiced
Conductor thickness embedding in between circuit	good	good	good	good	good	good	good	poor	poor	good	good
Surface smoothness on circuit (μm)	within ±3	within ±3	within ±3	within ±3	within ±3	within ±3	within ±3	with void	exposed circuit	not practiced	within ± 3
Solder heat resistance	good	good	good	good	good	good	good	not practiced	not practiced	expansion and peeling	good

The results of Examples 1 to 6 and Production Examples 1 to 8 apparently indicate that the coating of an internal-layer circuit pattern and/or the resin filling in superficial via hole can be integrally and simultaneously carried out in accordance with the present invention and that a multi-layer printed wiring board can be prepared at a high productivity by using the same. The results of Comparative Examples 1 and 2 indicate that so as to handle the epoxy resin composition of the present invention as film, the fluid component should importantly be within a range of 10 to 55 % by weight in the resin composition. The results of Comparative Production Example 1 additionally indicate that at a content of a resin with a softening point lower than the laminate temperature being less than 10 % by weight in the resin composition, even a higher laminate pressure can hardly embed resin with no void in the through-hole; if no component suppressing thermal fluidity during lamination was contained as in Comparative Production Example 2, good lamination could never be effected. If a scrubbing component with poor heat resistance and poor chemical resistance was contained at 40 % by weight or more as in Comparative Production Example 3, the resulting film could not be used practically as an inter-laminar insulation material, though the via strength of the resulting plated conductor could be procured. If the inorganic component was above 30 % by weight, furthermore, the via of a small diameter of 100 μm or less was fallen into poor shape, even after a process of CO_2 laser and UV laser, causing problems in terms of connection reliability; additionally, such resin composition had poor laser piercing property; for example, the resin composition caused the reduction of laser processing rate. If even a scrubbable resin composition containing a scrubbing component at 40 % by weight or more was prepared as an adhesive film of a two-layer structure as in Example 4 or 5, the via strength and reliability could be established concurrently in a simple manner.

By the method of the present invention, an inter-laminar adhesive film for multi-layer printed wiring boards can be prepared, embodiments of which may have excellent embedding property of the internal-layer circuit and excellent surface smoothness, and by using the adhesive film, a multi-layer printed wiring board can be produced by a build up process at a high productivity.

Embodiments of the invention were described herein by way of example only and with reference to the accompanying drawings of which:

Fig 1 shows the appearance of the adhesive film for multi-layer printed wiring boards of the present invention, which is formed on a support base film and is embedded in an internal-layer circuit board with a circuit pattern and a through-hole.

Fig 2 shows the appearance of the adhesive film for multi-layer printed wiring boards after the process of Fig. 1, at an embedded state in an internal-layer circuit board from which is peeled off a support base film, at a prestage to form a copper foil or a conductor layer through plating.

Fig 3 shows an appearance such that the scrubbable resin composition and the inter-laminar adhesive film for multi-layer printed wiring boards, formed on the support base film, are at a state of being embedded in the internal-layer circuit board with a circuit pattern and a through-hole.

Fig 4 shows an appearance of the adhesive film for multi-layer printed wiring boards after the process of Fig. 1, at an embedded state in an internal-layer circuit board from which is peeled off a support base film, at a prestage to form a copper foil or a conductor layer through plating.

[Description of the Symbols]

1. Support base film

2. Resin composition in solids at ambient temperature in the inter-laminar adhesive film for multi-layer printed wiring boards in accordance with the present invention

3. Internal-layer conductor layer

4. Internal-layer circuit board

5. Through-hole

6. Scrubbable resin composition or additive resin composition (resin composition for additive process)

Claims

1. A method of forming a laminate comprising applying an inter-laminar adhesive film to an internal-layer circuit board having an internal-layer conductor thereon, and laminating them at a lamination temperature, wherein the adhesive film comprises a support film base and a resin composition on the base, which composition is solid at ambient

temperature and which contains at least 10% by weight of a resin with a lower softening point than the lamination temperature, and the resin composition having a thickness greater than that of the conductor; whereby, on laminating at the lamination temperature, the extent of resin flow is at least of the thickness of the conductor, or is of the depth of a superficial via hole if present in the inter-layer circuit board, or is at least half the depth of a through-hole if present in the internal-layer circuit singly or in combination with a superficial via hole.

2. A method according to claim 1 wherein said resin composition contains inorganic components at a content of not more than 30% by weight.

3. A method according to claim 1 or claim 2 wherein the resin composition comprises:

(A) an epoxy resin liquid at ambient temperature;

(B) a polyfunctional epoxy resin with a softening point higher than the lamination temperature and with two or more epoxy groups within the molecule; and

(C) a latent epoxy curing agent initiating a reaction at a temperature higher than the lamination temperature; and wherein the resin composition may or may not contain a resin liquid at ambient temperature other than the component (A) and/or an organic solvent and wherein the resin liquid at ambient temperature including the component (A) and/or the organic solvent in total are at 10 to 55% by weight.

4. A method according to claim 1 or claim 2 wherein the resin composition comprises:

(A) an epoxy resin liquid at ambient temperature;

(B') a polyfunctional epoxy resin with a softening point lower than the lamination temperature and with two or more epoxy groups within the molecule; and

(C) a latent epoxy curing agent initiating a reaction at a temperature higher than the lamination temperature; and

(D) a binder polymer with a weight average molecular weight within the range 5,000 to 100,000; and wherein the resin composition may or may not contain a resin liquid at ambient temperature other than the component (A) and/or an organic solvent;

wherein the resin liquid at ambient temperature including the component (A) and/or the organic solvent in total are at 10 to 55% by weight; and
wherein the component (D) is at 5 to 50% by weight.

5. A method according to anyone of the preceding claims wherein the resin composition contains (E) at least one scrubbing component selected from a rubber component, an amino resin, an inorganic filler, and an organic filler, all soluble in oxidants, and
wherein the component (E) is at 5 to 40% by weight in the resin composition.

6. A method according to anyone of claims 1 to 4 wherein said inter-laminar adhesive film comprises a layer of a scrubbable resin composition solid at ambient temperature between the support film base and the resin composition solid at ambient temperature, the scrubbable resin composition comprising:

(A) a polyfunctional epoxy resin with two or more epoxy groups within the molecule;

(B) an epoxy curing agent; and

(C) at least one scrubbing component selected from the group consisting of a rubber component, an amino resin, an organic filler and an organic filler, which scrubbable resin composition may or may not contain an organic solvent.

7. A method according to any one of claims 1 to 5 wherein the resin composition contains at least one electroless plating catalyst (F) selected from metals, metal compounds and/or inorganic compositions absorbed or coated

with these electroless plating catalysts, and component (F) is at 0.05 to 3% by weight in the resin composition.

8. A method according to any one of claims 1 to 5 wherein said inter-laminar adhesive film comprises a layer of an additive resin composition solid at ambient temperature, between the support film base and the resin composition solid at ambient temperature, the additive resin composition comprising:

(A) a polyfunctional epoxy resin with two or more epoxy groups within the molecule;

(B) an epoxy curing agent; and

(D) at least one electroless plating catalyst selected from metals, metal compounds, and/or inorganic compositions absorbed or coated with these electroless plating catalysts.

9. A laminate as obtainable by the method of any one of claims 1 to 8 carried out under pressure and with heating while keeping the resin composition in contact with the internal layer circuit board.

10. A process for producing a multi-layer printed wiring board comprising peeling off the support base film from a laminate of claim 9 and laminating a copper foil on the optionally thermally cured adhesive layer by the use of heat or adhesive.

11. A process for producing a multi-layer printed wiring board comprising peeling off the support base film from a laminate of claim 9, optionally curing the adhesive film, subjecting the film to a piercing process by means of laser or drill, scrubbing the surface of the adhesive film by a dry process and/or a wet process, if necessary, and forming a conductor layer as an upper layer thereof by dry plating and/or wet plating.

12. A process for producing a multi-layer printed wiring board comprising peeling off the support base film from a laminate of claim 9 as dependent on claim 7 or claim 8, optionally curing the adhesive film, subjecting the film to a piercing process by means of laser or drill, scrubbing the surface of the adhesive film by a dry process or a wet process, if necessary, and forming a conductor layer as an upper layer thereof by electroless plating and/or electro plating.

13. A process for producing a multi-layer printed wiring board comprising repeating the process of any one of claims 10 to 12 plural times to laminate the resulting built up layer in multiple steps.

14. A multi-layer printed wiring board as obtainable by the process of any one of claims 10 to 13.

15. An inter-laminar adhesive film for use in the method of any of claims 1 to 8.

Fig. 1

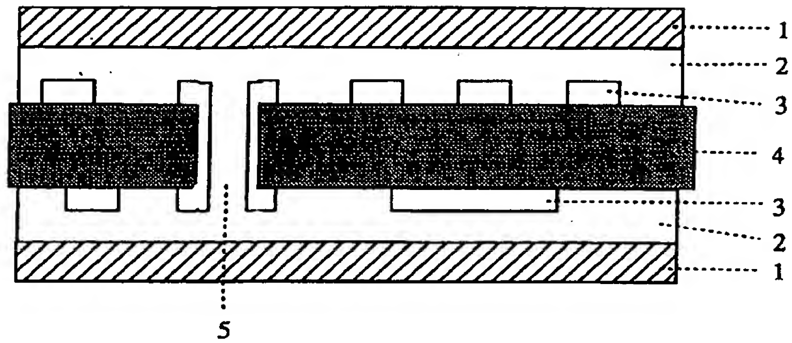

Fig.2

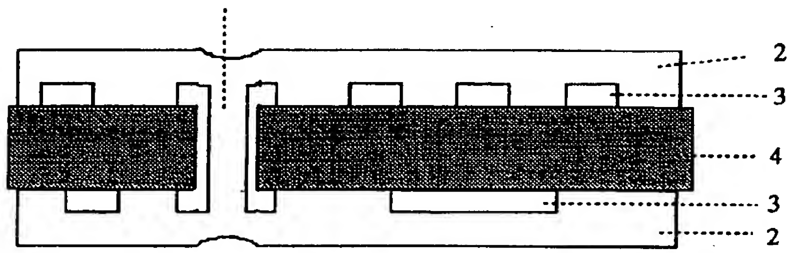

Fig.3

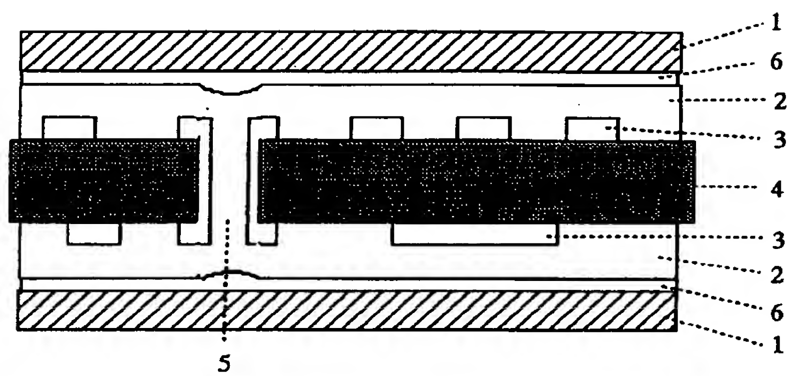

Fig.4